Ferroelectricity in ultrathin perovskite films

Na Sai, Alexie M. Kolpak, and Andrew M. Rappe

The Makineni Theoretical Laboratories, Department of Chemistry, University of Pennsylvania,

Philadelphia, Pennsylvania 19104-6323, USA

(Received 28 February 2005; published 7 July 2005)

We report studies of ferroelectricity in ultrathin perovskite films with realistic electrodes. The results reveal stable ferroelectric states in thin films less than 10 Å thick with polarization normal to the surface. Under short-circuit boundary conditions, the screening effect of realistic electrodes and the influence of real metal-oxide interfaces on thin film polarization are investigated. Our studies indicate that metallic screening from the electrodes is affected by the difference in work functions at oxide surfaces. We demonstrate this effect in ferroelectric $PbTiO_3$ and $BaTiO_3$ films.

PACS number(s): 77.80.−e, 77.84.Dy, 77.22.Ej

The effect of size on thin-film ferroelectricity has been known for a long time, but has not been completely understood. Initial experiments and mean-field calculations based on the Landau theory suggested that below a critical correlation volume[1] of electrical dipoles between 10–100 nm^3, ferroelectricity vanishes due to intrinsic size effects.[2,3] For thin films with the polar axis perpendicular to the surface, incomplete compensation of surface charges creates a depolarizing field that has been shown to further reduce the polarization stability.[4,5]

Recently, however, monodomain ferroelectric phases have been observed in very thin films, below 10-unit-cells thick.[6–8] Furthermore, Fong *et al.* showed that ferroelectric phases can be stable down to ~12 Å (3 unit cells) in $PbTiO_3$ films by forming 180° stripe domains, suggesting that no fundamental thickness limit is imposed by the intrinsic size effect in thin films.[9] This idea has been corroborated by *ab initio* calculations carried out on perovskite films, which indicate that no critical thickness exists for polarization parallel to the surface[10] and that polarization perpendicular to the surface can exist in films 3-unit-cells thick if the depolarization field is artificially removed.[11,12]

On the other hand, it has been found that the depolarization field plays a dominant role in reducing polarization normal to the surface and depressing ferroelectric transition temperatures in thin films. In a continuum model by Batra *et al.*,[4] which includes the depolarization effect, a critical thickness of 100 Å for perovskite films was analytically derived, assuming a Thomas-Fermi screening length of 1 Å for the metal electrodes. Also, a recent first-principles calculation revealed that $BaTiO_3$ films with $SrRuO_3$ electrodes lose ferroelectricity below ~24 Å (6 unit cells),[13] thus suggesting that a minimum thickness limit exists for useful ferroelectric films. While indeed a minimum film thickness must be influenced by the polarization of the ferroelectrics and the screening length of the electrodes,[14] it is not yet clear whether the depolarizing field can ever be completely removed by realistic electrodes on ultrathin films, nor how monodomain thin-film ferroelectricity is affected by the choice of electrodes and by the interactions at the metal-oxide interface.

In this paper, we provide answers to these questions. In particular, we investigate how the critical thickness varies in different systems with realistic electrodes. We find that even

though ferroelectricity is lost in $BaTiO_3$ thin films, polarization close to the bulk value can be stabilized in $PbTiO_3$ thin films with thicknesses less than 10 Å; the behavior in $BaTiO_3$ is therefore not universal to all ferroelectric thin films. Furthermore, we show that inequivalent ferroelectric-electrode interfaces can assist in stabilizing ferroelectricity in thin films.

We apply density functional theory (DFT) calculations[15] to ultrathin ferroelectric capacitors that are constructed of $PbTiO_3$ and $BaTiO_3$ films sandwiched between two conducting electrodes. Two electrodes commonly used in ferroelectric devices are studied: platinum (Pt) and the metallic oxide $SrRuO_3$. Short-circuit boundary conditions are imposed by the periodic boundary conditions and electrodes of sufficient thickness.

We consider AO (A=Pb or Ba) and TiO_2 ferroelectric terminations, and we examine different ferroelectric-electrode interfaces, focusing on the lowest energy one for each termination. Pt is most stable with the first layer situated above the oxygen atoms on the TiO_2 terminated surface, and above A and O atoms on the AO-terminated surface.[16] The periodically repeated supercells can thus be described by the general formula[17] $Pt_4/AO\text{-}(TiO_2\text{-}AO)_m/Pt_5$ and $Pt_4/TiO_2\text{-}(AO\text{-}TiO_2)_m/Pt_5$ with Pt electrodes, and $(SrO\text{-}RuO_2)_2/AO\text{-}(TiO_2\text{-}AO)_m/(RuO_2\text{-}SrO)_2\text{-}RuO_2$ and $(RuO_2\text{-}SrO)_2/TiO_2\text{-}(AO\text{-}TiO_2)_m/(SrO\text{-}RuO_2)_2\text{-}SrO$ with $SrRuO_3$ electrodes (periodic boundary conditions means that the ferroelectric slabs are separated by nine layers of electrode). Figure 1 shows the structures for two representative systems at $m=2$. Although ferroelectric instabilities can be present in the directions parallel and perpendicular to the film, here we focus only on the latter situation, as our primary interest is the depolarization effect. Therefore, for all the capacitors considered, the in-plane atomic positions are kept fixed at the ideal perovskite positions and the in-plane lattice constants are set equal to the experimental value for the corresponding bulk ferroelectric perovskite, i.e., a=3.935 Å for $PbTiO_3$, and a=3.991 Å for $BaTiO_3$.[18]

We start by determining the fully relaxed structures of the supercells. The atomic positions and strains are fully relaxed along the surface normal direction. Figure 1(a) shows the relaxed supercell structure of the TiO_2-terminated $PbTiO_3$
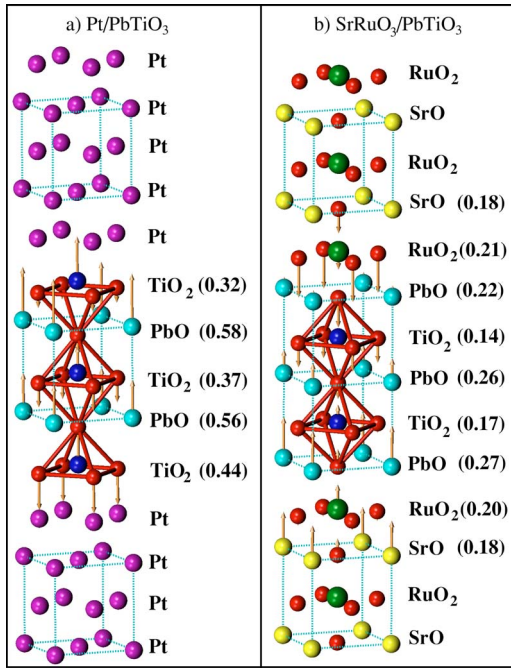
FIG. 1. (Color online) (a) TiO_2-terminated $Pt/PbTiO_3/Pt$ structure. (b) PbO-terminated $SrRuO_3/PbTiO_3/SrRuO_3$ structure. The ferroelectric displacement patterns are shown by arrows. The rumpling of each layer (displacement of cations relative to anions) is marked, in angstroms.

film with Pt electrodes and $m=2$. The displacements from the centrosymmetric structures are calculated. The relative displacement between the cations and anions for each $PbTiO_3$ layer [see Figure 1(a)] clearly demonstrates that the structure is in a ferroelectric state. As Table I shows, $PbTiO_3$ films with Pt electrodes are ferroelectric for all thicknesses down to $m=1$. For both terminations, the polarization values in these systems are slightly larger than the corresponding bulk value.[19]

These results suggest that bulk ferroelectric polarization can be stabilized in thin films below 10 Å with realistic electrodes. As Fig. 1 illustrates, an upward pointing polarization leads to an enhancement of the relative displacements at the bottom interface, and a reduction at the top interface, relative

TABLE I. Polarization (P) and tetragonality ratio c/a for $PbTiO_3$ films with Pt and $SrRuO_3$ electrodes. The bulk values are given in the last line.

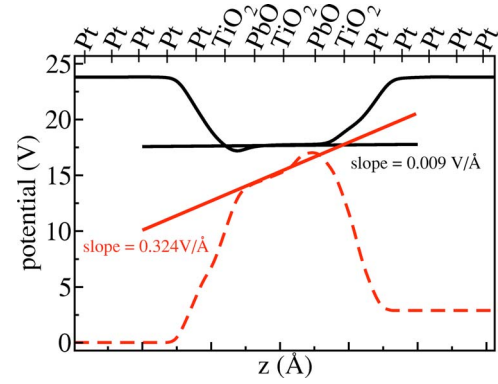| Termination	electrode	m	P (C/m^2)	c/a
PbO	Pt	1	0.89	1.109
PbO	Pt	2	1.00	1.140
PbO	Pt	4	0.88	1.058
TiO_2	Pt	2	0.86	1.110
TiO_2	Pt	4	0.85	1.055
PbO	$SrRuO_3$	2	0.36	1.049
TiO_2	$SrRuO_3$	2	0.32	1.040
		bulk	0.75	1.060

FIG. 2. (Color online) Macroscopic-averaged electrostatic potential along the film normal direction of the TiO_2-terminated $Pt/PbTiO_3/Pt$ capacitor (solid curve) and a freestanding $PbTiO_3$ slab with a fixed bulk ferroelectric displacement (dashed curve). The potential is constant inside the Pt electrodes.

to the interior layers. This observation is in agreement with previous DFT calculations with external fields.[12] In going from $m=2$ to $m=4$, both P and c/a decrease towards the bulk values as the surface-to-volume ratio decreases and the surface effect is averaged over more layers. To further check whether there exists a thickness limit below which ferroelectricity disappears in this system, we examine the structure at $m=1$. We find that a single unit cell has a stable polarization of 0.89 C/m^2, despite the stoichiometrically different environment as compared to bulk $PbTiO_3$.[9] We therefore find strong evidence for the absence of a critical thickness for ferroelectricity in $PbTiO_3$ films with Pt electrodes. In contrast to the $PbTiO_3$ films, none of the $BaTiO_3$ structures were found to be ferroelectric for $m=2$ or $m=4$, in agreement with the results in Ref. 13.

To make contact with earlier analytic theory,[4,14] we examine the electric field in the $Pt/PbTiO_3/Pt$ capacitor by plotting the macroscopic-averaged[20] electrostatic potential, as shown in Fig. 2. Also shown in Fig. 2 is the potential in the freestanding $PbTiO_3$ film in which a bulk ferroelectric displacement perpendicular to the surface is imposed.[21] The slope of the potential in the $PbTiO_3$ slab, which is the depolarizing field, is significantly smaller in the capacitor (0.009 V/Å), than in the freestanding slab (0.324 V/Å). Our calculations show that in the absence of electrodes, the latter field brings the system back to the paraelectric structure. The cancellation of a substantial fraction (97%) of the depolarizing field is due to metallic screening from the grounded electrodes that compensates the polarization charge.

In addition, the screening is accompanied by the formation of unequal local dipoles at the two interfaces due to different chemical bonding, as shown in Fig. 3. On the top interface, the Pt and Ti atoms lose charge, which is redistributed between the atoms, forming a Pt-Ti alloy. On the bottom interface, where the Pt-O distance is the shortest, the Pt and O atoms lose charge, the Pt from the d_{z^2} orbitals, and the O from the p_z orbitals,[22] while the Pt d_{xz} and d_{yz} orbitals gain charge. Similar behavior is observed at the ferroelectric-electrode interfaces of the AO-terminated capacitors. This inequivalent charge arrangement at the two ferroelectric-
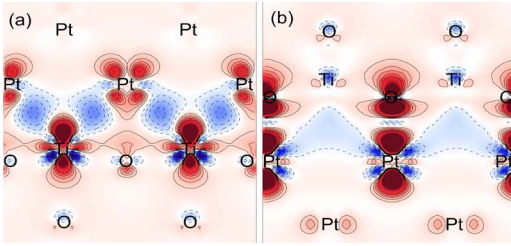
FIG. 3. (Color online) Contour plot of the induced charge density for the TiO_2-terminated $Pt/PbTiO_3/Pt$ capacitor structure at the (a) top interface (b) bottom interface. (The Pt layers farther from the interfaces are not shown.) Electron loss is given by solid lines and electron gain by dotted lines. The induced charge density is found by subtracting the charge densities of freestanding Pt and $PbTiO_3$ slabs from the total charge density in the capacitor.

metal interfaces is consistent with the different interface polarizations we noted earlier.

With $SrRuO_3$ electrodes, the heterostructures also adopt a ferroelectric state, as shown in Fig. 1(b). However, unlike with Pt electrodes, the polarization with $SrRuO_3$ electrodes is only half the bulk value, indicating that the surface charges are only partially compensated. The c/a ratio for the $SrRuO_3/PbTiO_3/SrRuO_3$ capacitor falls to 1.045 as the film thickness decreases to 2 unit cells. The corresponding electrostatic potential shows a depolarizing field of 0.07 V/Å across the $PbTiO_3$ slab, which is much smaller than in the freestanding $PbTiO_3$ film and explains why the polarization is stabilized at a significant level. Nevertheless, the stronger field compared to that in the $Pt/PbTiO_3/Pt$ structures also confirms the weaker screening effect of $SrRuO_3$ compared to Pt and other transition metals.[14]

We note further that allowing the internal coordinates of the $SrRuO_3$ electrodes, especially those in the boundary layers, to relax together with the $PbTiO_3$ ions is crucial. When the $SrRuO_3$ ions are fixed in their ideal positions, we find only paraelectric structures for either of the $PbTiO_3$ terminations. This result indicates that the interaction between the $PbTiO_3$ and the $SrRuO_3$ electrodes plays a crucial role in stabilizing ferroelectricity: the screening effect alone cannot account for the significant reduction of the depolarizing field.

The results presented so far have suggested that ferroelectric polarization normal to the surfaces can be stabilized in thin films less than 10 Å thick. However, they do not explain why the ferroelectric instability can be retained in $PbTiO_3$ but not in $BaTiO_3$ films when the same electrodes are applied. To address this question, we turn now to look at the depolarizing field and screening effects in these systems. The depolarizing field was previously addressed in phenomenological studies,[5,14,23] and is shown to scale with the spontaneous polarization of the ferroelectrics, the screening length of the electrodes and the inverse ferroelectric film thickness. Hence, the depolarizing field would be expected to be negligible only in very thick films.

In our calculations, inspection of the electrostatic potential in the freestanding film with a fixed bulk ferroelectric displacement shows that the potential drop across the ferroelectric slab (Δ_1) is different from the potential difference between the two asymptotic vacuum potentials (Δ_2), as illus-
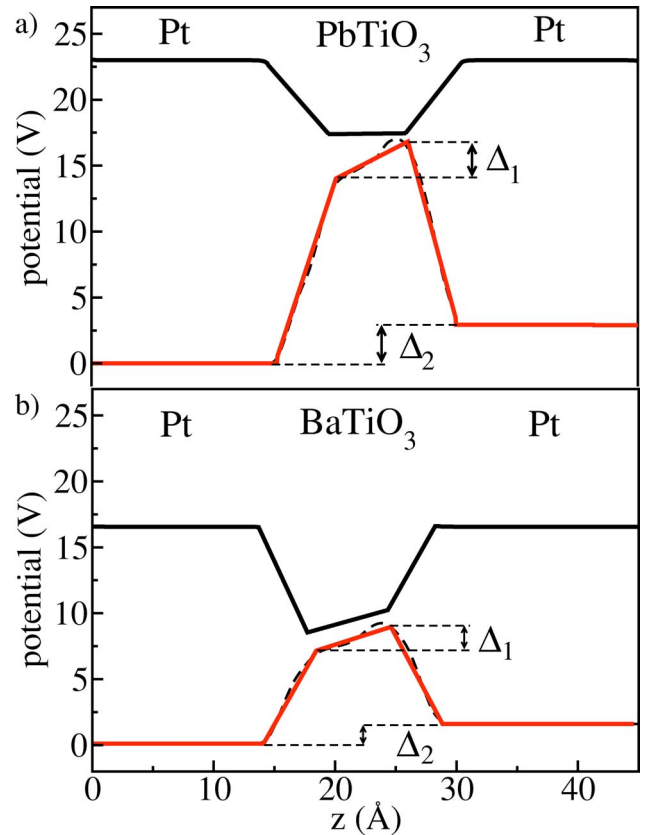

FIG. 4. (Color online) The electrostatic potential of a freestanding film with a fixed bulk ferroelectric displacement (lower curve); the self-consistent potential from solving the Poisson equation for Thomas-Fermi screening charges (upper curve). Panel (a) is $PbTiO_3$ film and panel (b) is $BaTiO_3$ film.

trated in Fig. 4. This difference arises because the two surfaces have different work functions, as a result of the polarization orientation, parallel to the top surface normal and antiparallel to the bottom one. Because Pauli repulsion keeps metal electrons out of the ferroelectric, the potential drop that is "seen" and screened by the electrodes is Δ_2, not Δ_1. An electrostatic analysis[24] of the potential and the electric field in the slabs shows that this difference must be taken into account when modeling the screening in all realistic systems.

We use a simple Thomas-Fermi model to highlight the effect of metallic screening on a ferroelectric slab, without the complex structural and electronic relaxations of DFT calculations. We treat the DFT macroaveraged electrostatic potential of the freestanding film as an initial potential and find the metallic screening charge using Thomas-Fermi theory. We then find the total self-consistent potential by solving the Poisson equation.[24] Figure 4 shows that in a $PbTiO_3$ slab of two unit cells, where $\Delta_2/\Delta_1 \sim 1.1$, metallic screening from the electrodes results in a potential that is close to constant in the $PbTiO_3$ slab. On the other hand, in a $BaTiO_3$ slab where $\Delta_2/\Delta_1 \sim 0.9$, a similar calculation yields a screening potential with a significantly larger depolarizing field. These Thomas-Fermi results can be explained as follows. Suppose that the metal screens a fraction f of the potential drop Δ_2. For $\Delta_2 > \Delta_1$, this translates into screening a larger fraction

$f\Delta_2/\Delta_1$ of the ferroelectric potential drop Δ_1. However, if $\Delta_2 < \Delta_1$, then the fraction of the ferroelectric potential drop, $f\Delta_2/\Delta_1$, is less than f. The difference in the polarization stability of ultrathin $PbTiO_3$ and $BaTiO_3$ films is therefore directly related to the relation of Δ_2 and Δ_1 for the two materials. We therefore emphasize the importance of the inequivalence of the work functions in determining the ferroelectric behavior of ultrathin films at this range of thickness.

In this paper, we have presented an *ab initio* demonstration of realistic electrodes stabilizing polarization normal to the surface in ultrathin films of <10 Å thick. We have shown that proper electrical and chemical boundary conditions are essential in stabilizing ferroelectricity. Using various electrodes, we find that monodomain ferroelectricity can persist down to one unit cell, suggesting that thin-film ferroelectrics are not specific to a single system. The ferroelectric polarization results in a difference in the work functions at oxide surfaces that must be considered in modeling the metallic screening. We demonstrate this difference in $PbTiO_3$ and $BaTiO_3$ films in which we find significantly different screening behaviors with the same electrodes.

[1] M. E. Lines and A. M. Glass, *Principles and Applications of Ferroelectrics and Related Materials* (Clarendon Press, Oxford, 1977).

[2] R. Kretschmer and K. Binder, Phys. Rev. B **20**, 1065 (1979).

[3] W. L. Zhong, Y. G. Wang, P. L. Zhang, and B. D. Qu, Phys. Rev. B **50**, 698 (1994).

[4] I. P. Batra and B. D. Silverman, Solid State Commun. **11**, 291 (1972).

[5] R. R. Mehta, B. D. Silverman, and J. T. Jacobs, J. Appl. Phys. **44**, 3379 (1973).

[6] A. V. Bune *et al.*, Nature (London) **391**, 874 (1998).

[7] T. Tybell, C. H. Ahn, and J.-M. Triscone, Appl. Phys. Lett. **75**, 856 (1999).

[8] C. Lichtensteiger, J. M. Triscone, J. Junquera, and P. Ghosez, Phys. Rev. Lett. **94**, 047603 (2005).

[9] D. D. Fong *et al.*, Science **304**, 1650 (2004).

[10] E. Almahmoud, Y. Navtsenya, I. Kornev, H. X. Fu, and L. Bellaiche, Phys. Rev. B **70**, 220102(R) (2004).

[11] P. Ghosez and K. M. Rabe, Appl. Phys. Lett. **76**, 2767 (2000).

[12] B. Meyer and D. Vanderbilt, Phys. Rev. B **63**, 205426 (2001).

[13] J. Junquera and P. Ghosez, Nature (London) **422**, 506 (2003).

[14] M. Dawber, P. Chandra, P. B. Littlewood, and J. F. Scott, J. Phys.: Condens. Matter **15**, L393 (2003).

[15] The calculations were performed within the generalized gradient approximation to the DFT as implemented in the DACAPO pacakge (http://www.fysik.dtu.dk/campos). We have used the ultrasoft pseudopotential [D. Vanderbilt, Phys. Rev. B **41**, 7892 (1990)].

[16] The Pt electrodes can be oriented to form Pt (100) or Pt (111) on the (100) surface of perovskites. However, we choose to focus on the Pt (100) surface, as the orientation does not affect the screening properties.

[17] The slabs all have access to a paraelectric state with perfect inversion symmetry; this ensures that ferroelectricity is due only to spontaneous symmetry breaking.

[18] When slightly smaller in-plane lattice constants of substrate materials such as $SrTiO_3$ are used instead, all c/a ratios are increased slightly compared to the values shown in Table I.

[19] Polarizations were computed by finding the ratio of the thin film and bulk displacement amplitudes, then multiplying by the bulk spontaneous polarization.

[20] The macroscopic-averaging [A. Baldereschi, S. Baroni, and R. Resta, Phys. Rev. Lett. **61**, 734 (1988)] is obtained by convolving the planar-averaged potential (in the x-y plane) with a window function in the z direction using the $PbTiO_3$ and Pt lattice constants for the window parameter. We select to focus on $m = 2$ in this analysis as it is the smallest structure that has a center region one unit cell wide (≈ 4 Å).

[21] This system can be realized by imposing the atomic displacement of the bulk ferroelectric state in the center of a slab, and relaxing the surface layers structure. The slope of the potential is determined by the band gap and thickness of the ferroelectric.

[22] F. Y. Rao, M. Y. Kim, and A. J. Freeman, Phys. Rev. B **55**, 13953 (1997).

[23] I. P. Batra, P. Wurfel, and B. D. Silverman, Phys. Rev. Lett. **30**, 384 (1973).

[24] A. M. Kolpak, N. Sai, and A. M. Rappe (unpublished).